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Author(s):
Casapu, Maria; Grunwaldt, Jan-Dierk; Maciejewski, Marek; Baiker, Alfons; Hoyer, Ruediger; Wittrock, Meike; Eckhoff, Stephan

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Enhancement of Activity and Self-reactivation of NSR-catalysts by Temporary Formation of $BaPtO_3$-perovskite

Maria Casapu · Jan-Dierk Grunwaldt · Marek Maciejewski · Alfons Baiker · Rüdiger Hoyer · Meike Wittrock · Stephan Eckhoff

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Abstract Calcination of a $Pt/Ba/CeO_2$ catalyst at 700 °C and subsequent reduction in hydrogen, carbon monoxide or propene at 350–550 °C resulted in a considerable improvement of its NO_x storage-reduction (NSR) properties compared to those of a freshly prepared $Pt/Ba/CeO_2$ catalyst. This behavior is traced back to the temporary formation of $BaPtO_3$ perovskite which leads after reduction to well-distributed Pt particles in intimate contact with the barium-containing phases. The oxidation and reduction of platinum is reversible which can be exploited for the design of "self-regenerating" NSR-catalysts under lean (>600 °C) and rich (>400 °C) reaction conditions. The formation of the $BaPtO_3$-perovskite may not only be interesting for NSR-catalysis, but generally for Pt-based catalysts where a high dispersion of Pt is important.

Keywords NO_x storage-reduction catalyst · NO_x removal · Perovskite · Self-regeneration · Aging · X-ray absorption spectroscopy · Pulse thermal analysis

M. Casapu · J.-D. Grunwaldt (✉) · M. Maciejewski · A. Baiker (✉)
Department of Chemistry and Applied Biosciences, Institute for Chemical and Bioengineering, ETH Zurich, Hönggerberg, Zurich 8093, Switzerland
e-mail: grunwaldt@chem.ethz.ch

A. Baiker
e-mail: baiker@chem.ethz.ch

R. Hoyer · M. Wittrock · S. Eckhoff
Umicore AG & Co. KG, Rodenbacher Chaussee 4, 63403 Hanau-Wolfgang, Germany

1 Introduction

One of the challenges in noble metal based catalysis is to achieve a high dispersion of the noble metals not only after preparation but also after many operating cycles [1]. This is particularly important in exhaust gas catalysis where one of the most stringent problems is the deterioration of the catalytic activity due to sintering of metal particles at high temperatures [2–4]. Usually, supports with high surface area and high thermal stability are applied, but this cannot suppress the growth of the precious metal particles during operation [1]. Moreover, much effort has to be done to finely disperse the noble metal in freshly prepared catalysts. An alternative promising strategy is to form noble metal perovskites [5]. The periodic incorporation of the metal into the perovskite lattice under oxidizing conditions and migration out of the perovskite upon reducing conditions is characteristic for a self-regeneration behavior, as already reported in three way catalysis [6, 7]. Most of the studies have been reported on Pd catalysts, whereas only a few investigations considered the use of this strategy also for Rh- or Pt-containing catalysts [8, 9]. Moreover, this concept has not been applied yet on NO_x storage-reduction (NSR) catalysts, including the preparation of highly dispersed Pt particles.

NSR catalysts normally contain noble metals (Pt, Rh) for the oxidation of NO to NO_2 (under lean fuel conditions) and the reduction of stored NO_x (under rich conditions), and a storage component deposited on carrier oxides with a high surface area, such as La_2O_3-stabilized γ-Al_2O_3 or CeO_2 [10]. Recently, we have studied the fate of Pt during ageing of $Pt–Ba–CeO_2$ catalysts and observed the formation of Pt-containing perovskites ($BaPtO_3$ and, at higher temperatures, Ba_2PtCeO_6) leading to a deactivation of $Pt/Ba/CeO_2$ catalysts [11]. In this letter we show that the

formation of Pt-based perovskites can be beneficially applied for preparing NSR-catalyst with highly dispersed Pt in intimate contact with barium. In addition, this type of catalysts can be regarded as "self-regenerating" catalysts.[1] At first, the formation of $BaPtO_3$ in Pt/Ba/CeO_2 catalysts at 700 °C is reported. Then we show the formation of metallic Pt species by reduction in H_2, C_3H_6 or CO under moderate conditions. The NSR performance of the catalysts prepared by the formation of the perovskite framework followed by its reduction is shown to be better than that of a freshly prepared Pt–Ba–CeO_2 catalyst. Finally, also the re-oxidation of metallic Pt particles and their reduction was tested to demonstrate that such temporary $BaPtO_3$ formation under oxidizing conditions may inhibit sintering of Pt particles if lean and rich cycles are used alternately, as it is typical for NSR catalysts.

2 Experimental

2.1 Sample Preparation

A Pt/Ba/CeO_2 catalyst with the nominal composition 0.74 wt.%Pt/15.5 wt.%Ba/CeO_2 (note that Pt is present as metallic Pt or PtO_x while Ba is in the form of BaO, $BaCO_3$ or $Ba(OH_2)$) was prepared by incipient wetness impregnation of the commercial ceria (Umicore) support with aqueous solutions of dinitrodiamine platinum (Strem Chemicals) and barium acetate (Umicore) as described in a previous paper [12]. After every impregnation step the sample was dried overnight at 80 °C and then calcined in air at 500 °C for 5 h. The sample is denoted in the following as 0.74-Pt/Ba/CeO_2. Additionally, a high noble metal loaded sample with the nominal composition 7.4 wt.%Pt/14.4 wt.%Ba/CeO_2 was prepared using the same procedure, denoted in the following as 7.4-Pt/Ba/CeO_2. This sample was used as a reference system which could be investigated by further techniques applied for investigation of bulk properties, e.g. X-ray diffraction. Finally, the in a special way thermally treated catalysts were obtained by calcination of the fresh catalysts at 700 °C for 12 in an ambient atmosphere. These samples are denoted as calc-0.74-Pt/Ba/CeO_2 and calc-7.4-Pt/Ba/CeO_2.

2.2 Characterization Techniques

Thermal Analysis (TA and PulseTA [13]) was performed on a Netzsch STA 409 thermoanalyser equipped with a pulse device enabling injection of a certain amount of one or two pure gases or gaseous mixtures into the He carrier gas stream flowing through the system. The sensitivity of the applied thermobalance is 1–2 μg. The outlet of the thermoanalyser was connected by a heated (ca. 150 °C) stainless steel capillary to a mass spectrometer (Pfeiffer Vacuum OmniStar).

The temperature programmed reaction experiments were carried out in an inert atmosphere (He) using ca. 70.0 mg sample. Prior to each experiment the samples were heated up to 500 °C with a heating rate of 10 °C/min for removal of all physisorbed species. NO_x storage-reduction tests were performed at 300 °C. The NO_x storage step was simulated using O_2 and NO pulses (3 ml O_2 and 2 ml NO for each cycle) injected into the carrier gas stream of 50 ml/min. The regeneration of the catalyst was done with 1 ml pulses of C_3H_6.

X-ray diffraction measurements were carried out on a standard powder X-ray diffractometer (Siemens D5000) using the Cu K_α radiation in the step scanning mode (step size of 0.01° and 2 s per step) between $2\Theta = 15$ and 65°. The pattern intensities were standardized by comparison with the intensity of Cu (111) reflection at $2\Theta = 43.178°$ as inert standard.

XANES and EXAFS experiments were performed at the beamline X1 at HASYLAB in Hamburg, Germany, and the setup has been described in [14]. In brief, XANES and EXAFS data were collected in the fluorescence and transmission mode using an in situ cell with X-ray fluorescence and transmission windows. The fluorescence X-rays of platinum were collected with a five-element Ge solid-state detector. Spectra were taken around the Pt L_3-edge (11.564 keV), using a Pt foil as reference for energy calibration. The outlet of the cell was connected to a mass spectrometer (Pfeiffer Vacuum OmniStar). For data evaluation the WINXAS 3.1 software was used [15].

3 Results

3.1 Formation of $BaPtO_3$ Perovskite

Figure 1 shows X-ray diffraction patterns of a fresh 7.4-Pt/Ba/CeO_2 sample and of the corresponding sample which was calcined at 700 °C (calc-7.4-Pt/Ba/CeO_2). Note that in this case the high loaded Pt-sample was used to follow the structural changes with respect to $BaPtO_3$ formation. For comparison, also the XRD patterns of a reference containing $BaPtO_3$ (prepared by calcinations at the same temperature of a $BaCO_3$–PtO_2 mechanical mixture in a 1:1 molar ratio) are presented. The XRD patterns show that there is no $BaPtO_3$ in the freshly prepared 7.4-Pt/Ba/CeO_2 sample, whereas a significant amount of $BaPtO_3$ was

[1] In the following we will use „self-reactivation" instead of "self-regeneration" to distinguish it from the regeneration step of the NSR process.

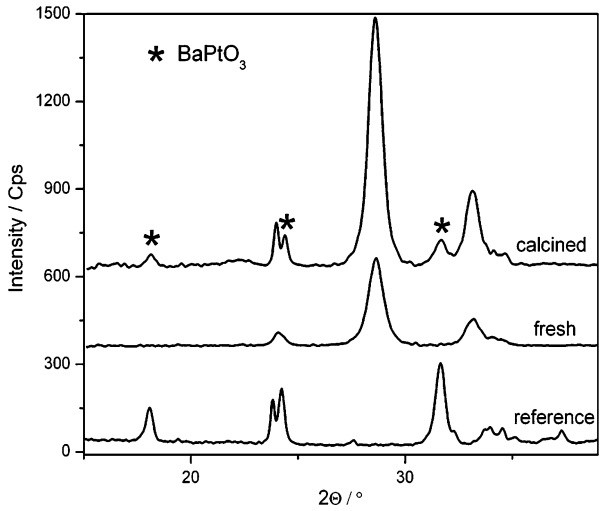

Fig. 1 X-ray diffraction patterns of fresh 7.4-Pt/Ba/CeO_2, calc-7.4-Pt/Ba/CeO_2 (calcined 12 h at 700 °C) and a reference sample containing $BaPtO_3$ (prepared by calcination of a 1:1 $BaCO_3$–PtO_2 mechanical mixture at 700 °C for 12 h); only the main reflections of $BaPtO_3$ are labeled; the others stem mainly from ceria (see text)

formed in the sample calcined at 700 °C. Additionally, the growth of CeO_2 and $BaCO_3$ crystallites during exposure to high temperatures led to the sharpening of their characteristic XRD reflections. A more detailed investigation of the reaction between PtO_x and $BaCO_3$ is given in ref. [11] which showed that above 800 °C a further reaction to the double perovskite Ba_2PtCeO_6 occurs. XAS studies on the lower loaded calc-0.74-Pt/Ba/CeO_2 sample revealed that Pt is in fully oxidized state after calcination at 700 °C. This is also in this case due to $BaPtO_3$ formation, since without Ba species in the system PtO_x is decomposed under these conditions. The formation of $BaPtO_3$ leads to an excellent distribution of platinum over the catalyst, but the NSR activity is significantly deteriorated.

3.2 Stability of $BaPtO_3$ Under H_2, CO or C_3H_6 Reducing Atmosphere

In order to restore the NO_x storage-reduction activity, Pt must migrate out of the perovskite framework; therefore in a next step the reduction behavior of both, low loaded calc-0.74-Pt/Ba/CeO_2 and high loaded calc-7.4-Pt/Ba/CeO_2 was monitored. TA-MS techniques were used to study the reduction of $BaPtO_3$ in the calc-7.4-Pt/Ba/CeO_2 samples while for calc-0.74-Pt/Ba/CeO_2 in situ fluorescence XAS measurements at the Pt L_3 edge were performed.

The calc-7.4-Pt/Ba/CeO_2 sample was exposed in the thermoanalyzer to 10%H_2, 10%CO or 10%C_3H_6 in helium upon heating (ramp 10 °C/min). In all cases the reduction of $BaPtO_3$ was observed below 400 °C. The TG-MS data indicate an increase of the reduction temperature in the order $H_2 < CO < C_3H_6$ (not shown). However, the exact determination of the temperature range of reduction is very difficult when using CO or propene as reducing agents. The reduction of the perovskite is overlapped by the disproportionation of CO or cracking of propene, resulting in deposition of carbon (CO), and coke and graphite (C_3H_6), respectively. Both these phenomena render the exact determination of the reduction temperature difficult. The XRD measurements performed after the TPR experiments confirmed the reduction of platinum in $BaPtO_3$ after exposure to each reducing atmosphere by the disappearance of the characteristic X-ray diffraction lines of $BaPtO_3$ and the appearance of platinum reflections (Fig. 2). The difference in the XRD patterns of the sample reduced by H_2, CO and C_3H_6 may result from their different reduction potential and possibly different reduction mechanism. In the case of propene and CO, the reduction of $BaPtO_3$ is superimposed by propene cracking and disproportionation of CO. Both solid products of these additional reactions can also reduce the $BaPtO_3$, which therefore may influence the reduction process. Moreover, the crystallization and coalescence of metallic Pt may be different under different atmospheres.

In a next step, the stability of $BaPtO_3$ in calc-0.74-Pt/Ba/CeO_2 was studied. Instead of XRD, in this case in situ fluorescence-XAS measurements at the Pt L_3-edge (cf. Fig. 3) were used due to the low concentration of Pt. The strong whiteline of the catalyst treated at 700 °C supports the conclusion that Pt was in fully oxidized state. The reduction of platinum in the catalyst was analyzed by taking XANES spectra every 5 min during heating the sample with 5 °C/min under 5%H_2/Ar (Fig. 3a) and 2.5%C_3H_6/He (Fig. 3b). The decrease of the whiteline

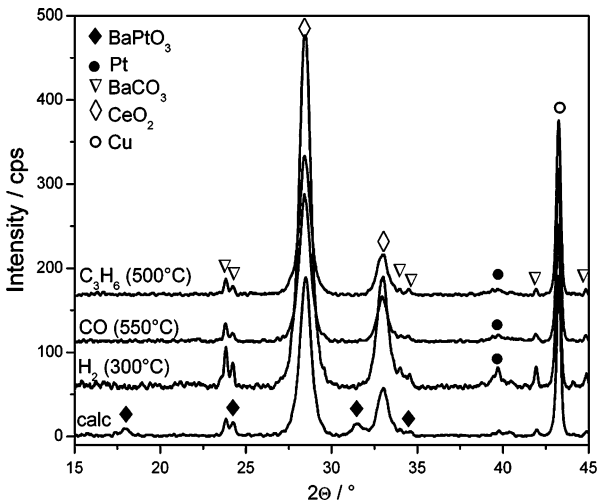

Fig. 2 XRD patterns recorded for the calc-7.4-Pt/Ba/CeO_2 catalyst before and after thermal analysis in 10 vol. %H_2, CO or C_3H_6

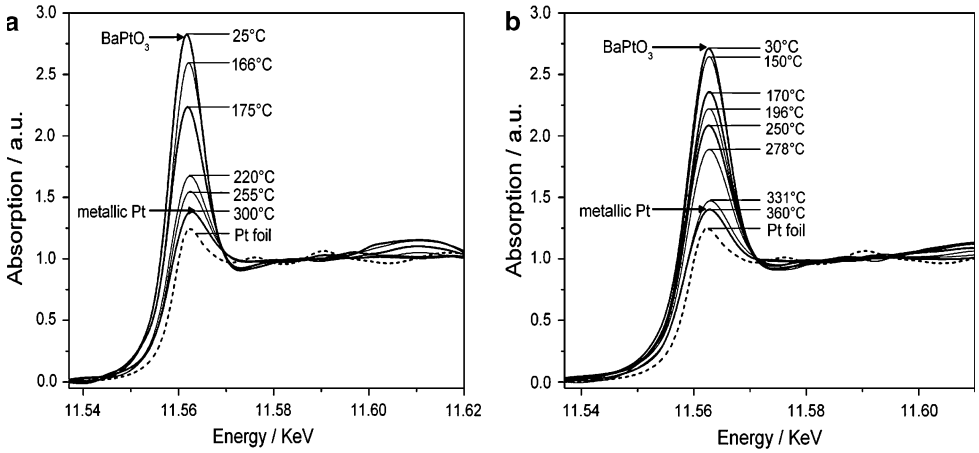

Fig. 3 In situ XAS measurements at the Pt L_3 edge during heating of the calc-*0.74*-Pt/Ba/CeO_2 catalyst with 5 °C/min in 5%H_2/Ar (**a**) and 2.5%C_3H_6/He (**b**). Conditions: ca. 100 mg sample, flow of 30 ml/min

intensity (which reflects the vacancy in the 5 d orbital of Pt atom) indicates a gradual reduction of platinum from Pt^{4+} to metallic state, occurring from ca. 150 °C. The results confirm the reduction of $BaPtO_3$ and a faster reaction with H_2 as observed for calc-7.4-Pt/Ba/CeO_2, which was investigated by TA-MS and XRD.

3.3 The NO_x Storage-reduction Behavior of the Aged and Reactivated 0.74-Pt/Ba/CeO_2 Catalyst

Figure 4 shows the NO_x storage-reduction activity of the fresh calc-0.74-Pt/Ba/CeO_2 and calc-0.74-Pt/Ba/CeO_2 catalysts after reduction at 400 °C with 1 ml H_2 pulses (4 pulses). The catalysts were investigated after 1, 3 and 10 NO/O_2 cycles and a corresponding regeneration pulse of 1 ml propene. This experimental procedure allowed the study of both the NO_x storage capacity and the effectiveness of the regeneration step after partial or complete saturation of the NO_x storage active sites. Note that the observed mass changes during storage were the sum of two processes: $Ba(NO_3)_2$ formation and $BaCO_3$ decomposition while the mass loss during regeneration with C_3H_6 is the result of the opposite reactions. The direct comparison of the two samples in Fig. 4 demonstrates that the performance of the catalyst treated according to the special procedure (calcination at 700 °C in air and reduction at 400 °C) is significantly improved compared to the fresh catalyst. The mass uptakes due to the NO_x storage for the fresh 0.74-Pt/Ba/CeO_2 catalyst after one, three and ten NO/O_2 cycles amount to 0.45, 0.90 and 1.96 mg, respectively, whereas the same amount (70 mg) of the calcined and reduced catalyst stored 0.54, 1.18 and 2.06 mg after one, three and ten NO/O_2 cycles, respectively. These differences correspond to 20.0% and 31.6%, respectively. Moreover, the regeneration step of the catalyst is substantially enhanced. 1 ml of C_3H_6 lead to the removal of 76% of the stored NO_x after ten NO/O_2 cycles (saturation

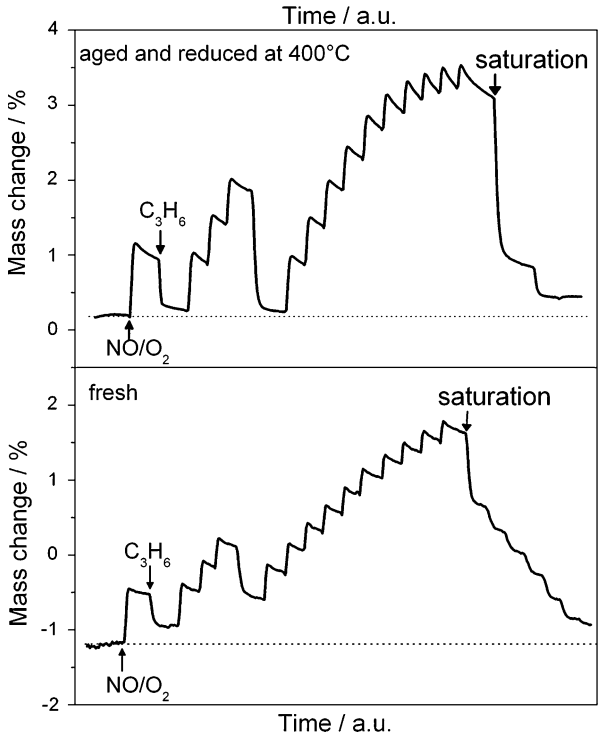

Fig. 4 NO_x storage-reduction activity at 300 °C of the fresh 0.74-Pt/Ba/CeO_2 and calc-0.74-Pt/Ba/CeO_2 reduced with H_2 pulses at 400 °C. Observed mass gains result from the NO/O_2 pulses, mass losses from the pulses of C_3H_6

of the NO_x storage sites) in the calcined and reduced 0.74-Pt/Ba/CeO_2 catalyst, whereas only 32% of the stored NO_x was reduced in the fresh 0.74-Pt/Ba/CeO_2 catalyst after ten NO/O_2 cycles.

In order to find the optimal reduction temperature of calc-0.74-Pt/Ba/CeO_2, the sample was subjected to a reducing hydrogen atmosphere in the thermal analyzer at selected temperatures in the range of 300–550 °C. For this purpose, four 1 ml pulses of H_2 were injected over the sample using He as carrier gas (50 ml/min). The results are

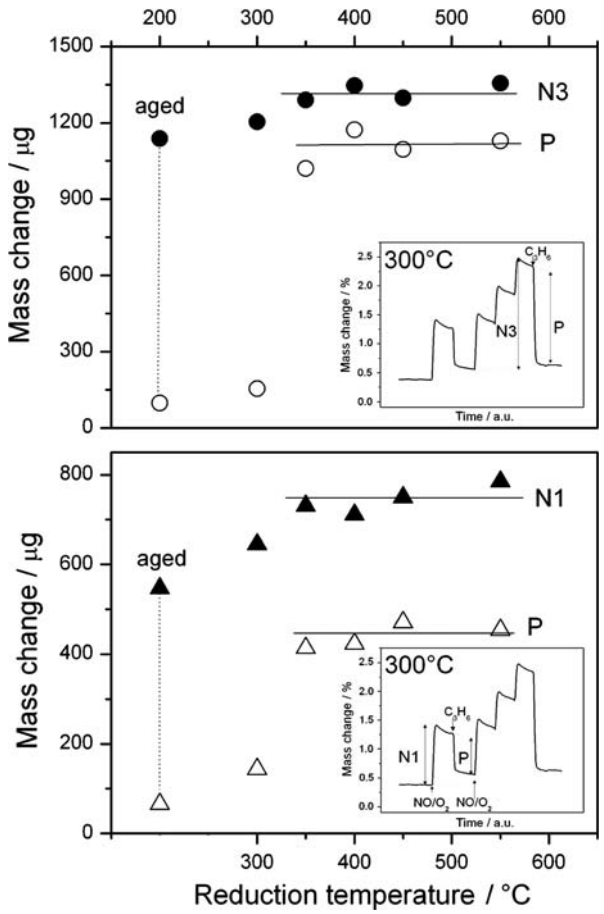

Fig. 5 Mass changes of the calc-0.74-Pt/Ba/CeO_2 catalyst resulting from one (top) or three (bottom) NO_x storage cycles at 300 °C (denoted in the inset as N1 and N3, respectively) and reduction with 1 ml of C_3H_6 (P in the inset) as a function of the temperature of reactivation by H_2

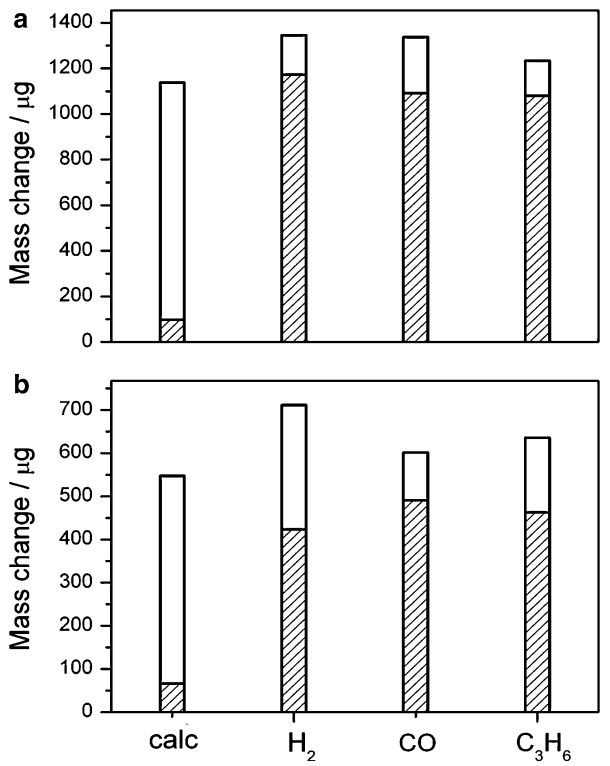

Fig. 6 Mass changes of the reactivated 0.74-Pt/Ba/CeO_2 catalyst resulting from one (**a**) or three (**b**) NO/O_2 cycles and 1 ml of C_3H_6 (dashed) at 300 °C as a function of the reactivation by four 1 ml pulses with different reducing agents at 400 °C: H_2, CO or C_3H_6. For comparison the results obtained for the calc-0.74-Pt/Ba/CeO_2 sample are shown as well

shown in Fig. 5. The insets of the figure explain the method of the determination of the storage capacities "N1" and "N3" as well as the yield of the regeneration process during the propene pulse (denoted as "P"). Reduction above 300 °C leads to an improvement of the NO_x storage and restoring of the regeneration activity. The NSR efficiency is similar for all samples reduced between 350 °C and 550 °C. These results show that the reduction of $BaPtO_3$, obtained by calcination at 700 °C, is necessary to reactivate the catalysts. The procedure may be also applied during catalyst preparation to obtain a better dispersion of Pt particles and thus improved NSR properties of 0.74-Pt/Ba/CeO_2 catalyst.

Additional NSR experiments were performed in the same way after reduction of $BaPtO_3$ in the calc-0.74-Pt/Ba/CeO_2 with propene and carbon monoxide instead of hydrogen (4 ml, reduction temperature 400 °C). Figure 6 summarizes the results during NO_x storage and during regeneration. Consistent with the results presented in Section 3.2, also after reduction in these atmospheres the NSR-performance increased significantly. The catalysts reactivated by exposure to CO or C_3H_6 showed a similar NO_x storage and reduction activity as that observed after reactivation with H_2 pulses at 400 °C.

In order to check whether the oxidation and reduction of Pt are reversible over more than one cycle, the NSR activity of the 0.74-Pt/Ba/CeO_2 catalyst was investigated after an additional calcination (air 700 °C) and reactivation (H_2 pulses, 400 °C) treatment (Fig. 7). Again the NSR performance deteriorated upon calcination and improved after reduction, indicating that the recurring formation and decomposition of $BaPtO_3$ during exposure to oxidizing and reducing atmosphere, respectively, is reversible. Similar values of the NSR activity, characterized by the mass changes during NO_x uptake and reduction, were obtained which corroborated the notable potential of the cycling process of temporary incorporation of Pt and its subsequent migration out (exfoliation) of the perovskite structure and the "self-reactivation" behavior.

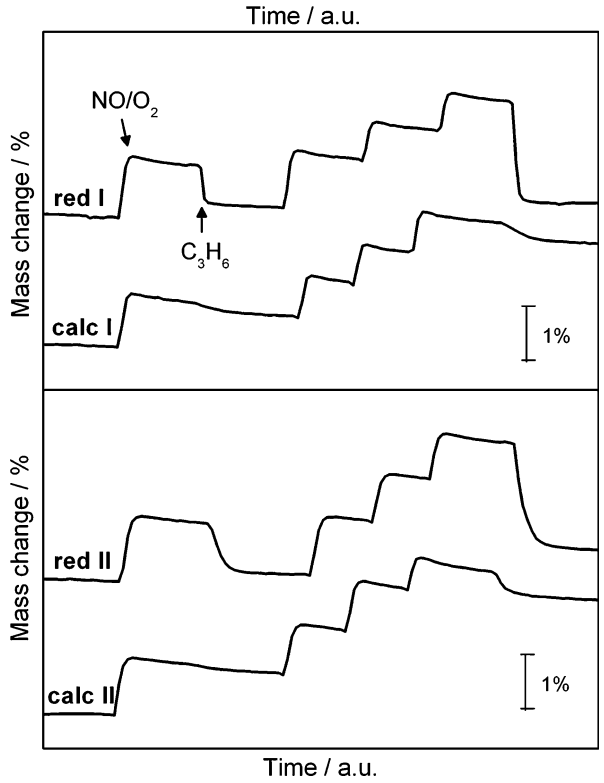

Fig. 7 Mass changes of the 0.74-Pt/Ba/CeO_2 catalyst resulting after one or three NO_x storage cycles (mass uptake due to NO/O_2 pulses) and reduction with 1 ml of C_3H_6 (mass loss) at 300 °C after calcinations at 700 °C (calc) and reduction at 400 °C with 4 ml H_2. The upper part of the figure presents the NSR activity of the catalyst after one (I), the bottom part after two (II) perovskite formation-reduction cycles

4 Discussion

In the present study we have shown that the $BaPtO_3$ perovskite can be formed under oxidizing conditions (here under air) and reduced again between 350–550 °C in hydrogen, carbon monoxide or propene. The NSR behavior of the 0.74-Pt/Ba/CeO_2 catalyst, under the model gas composition applied in the present study, is much improved by the specific thermal treatment leading to formation and reduction of perovskite $BaPtO_3$, compared to the catalyst obtained at significantly lower temperatures by simply decomposing precursors (Fig. 4). This behavior may be explained by the good dispersion of Pt particles in the catalyst and the achievement of a very high proximity of Pt and Ba species. The good dispersion of noble metal particles will provide a higher number of metallic Pt sites, while an intimate contact between Pt and Ba species may improve both the NO_x storage and regeneration processes. The beneficial effect obtained from the presence of Pt in the proximity of Ba species was also discussed by other groups [3, 16–20]. It seems that the enhanced spillover of NO_x and reducing species between the surfaces of the two components during storage and reduction led to the observed increase of the NSR activity.

The reversible formation of $BaPtO_3$, during exposure to alternating oxidizing and reducing atmosphere, may be also exploited to reactivate the catalyst and to protect Pt against sintering. Due to the fact that lean and rich cycles are used in NSR catalysis, this could also be used for "self-reactivation" of NSR catalysts at 700 °C. Such "self-reactivation" has been widely reported for Pd-based catalysts [6, 7], but much less for Pt-based materials, where only perovskites like $(La_{0.7}Sr_{0.2}Ba_{0.1})ScO_{3-x}$ [9], $LaFe_{0.95}Pt_{0.05}O_3$ and $CaTi_{0.95}Pt_{0.05}O_3$ [8] have been mentioned. In addition, higher temperature (800 °C both for oxidation and reduction, [6–8]) were used and, to our knowledge, this concept has not been reported in NSR catalysis yet. In this respect $BaPtO_3$, Ba_2PtCeO_6 and related perovskites are particularly attractive, since their components are interesting materials for NSR catalysis.

5 Conclusions

The formation of $BaPtO_3$ and its reduction by hydrogen, carbon monoxide or hydrocarbons provides interesting opportunities for NSR catalysis:

(I) The procedure seems to be beneficial for preparing well-distributed platinum in good contact with the NO_x-storage material. The activity of the reactivated catalyst is higher than that observed for a catalyst freshly prepared by impregnation and precursor decomposition.

(II) The formation of $BaPtO_3$ can be beneficially used for the design of a "self-reactivating" catalyst in which the formation of $BaPtO_3$ prevents sintering of Pt under oxidizing atmosphere (>700 °C), while during exposure to fuel rich or reducing conditions metallic Pt is released again from the lattice. Especially the conditions of this last reactivation process are milder than typically reported for "self-reactivating" catalysts in the literature.

(III) The formation of $BaPtO_3$ may also be used to redisperse platinum particles in aged catalysts.

Finally, the study may initiate the application of Barium as structural promoter required for the formation of Pt perovskites also in other areas where oxidizing and reducing conditions can be alternated and where Pt-dispersion plays an important role. Further studies will be required to follow the dispersion of Pt in more detail.

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